Lattice-matched heterostructures as Schottky barriers: HgSe/CdSe

J. S. Best[a] and J. O. McCaldin

California Institute of Technology, Pasadena, California 91125

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A novel structure, which is both a lattice-matched heterostructure and a Schottky barrier, is fabricated by epitaxial growth of (111) oriented HgSe on (0001) oriented CdSe. Hydrogen transport CVD is used, with a HgSe source temperature of 420°C and a CdSe substrate temperature of 330°C. Single crystal growth was obtained. Of the two orientations possible for the crystal symmetries involved, only one was observed for a given specimen. The "Schottky barrier" height for this lattice-matched heterostructure is 0.73 ± 0.02 eV as measured by the photoresponse method. This uncertainty is substantially less than is usual for Schottkies. The magnitude is greater by about one-quarter volt than is achievable with the most electronegative elemental metal, Au, in qualitative agreement with work function arguments.

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INTRODUCTION

The structure of the interface between a metal and a semiconductor, as usually fabricated, is complicated. Metal deposition can disrupt the surface of the semiconductor.[1] Bonding on either side of the interface differs drastically and, indeed, new thermodynamic phases may occur at such interfaces. On the other hand, lattice-matched heterostructures, such as $Al_xGa_{1-x}As/GaAs$, are relatively simple.

The mercury–chalcogenide/cadmium–chalcogenide interface is a unique "Schottky barrier" in that it is also a lattice-matched heterostructure. The tetrahedrally coordinated compounds Hg*X*, where *X* is S, Se, or Te, are semimetallic, and each has the same interatomic spacing as the corresponding Cd*X* semiconductor. Hg*X*/Cd*X* interfaces can therefore be grown as lattice-matched heterostructures. Thus, the Hg*X* provides a Schottky-like contact to the Cd*X* without the structural complexity that causes difficulty in understanding metal–semiconductor interfaces.

We report here the fabrication and electrical characterization of a HgSe/*n*-CdSe lattice-matched Schottky barrier contact. This system is the easiest of the mercury–chalcogenide/cadmium—chalcogenide heterostructures to grow by the CVD technique; and results can be compared with earlier work on nonepitaxial, polycrystalline HgSe contacts.

EPITAXIAL GROWTH

CdSe has a hexagonal, wurzite structure. HgSe has a cubic, zincblende structure. The two structures differ in the stacking sequence of hexagonal close packed planes. Because the nearest neighbor spacing is the same for HgSe as for CdSe, there is a lattice-match between the CdSe basal plane and the HgSe(111) plane. The actual amount of lattice mismatch at room temperature is only 0.08%.[2]

Growth of HgSe on *n*-CdSe was achieved using H_2 transport chemical vapor deposition. The two-zone furnace used for growth is schematically illustrated in Fig. 1, along with the reaction primarily responsible for transport. Deposition takes place under near equilibrium conditions.

Substrates were prepared from an undoped CdSe boule which was oriented and sliced to within 1/2° of basal plane. The Cd face of each slice was mechanically lapped and then polished in bromine–methanol solution. The polycrystalline HgSe source material was formed by direct reaction of the elements in an evacuated quartz capsule.

Initially, the source sat outside the hot zone of the furnace, and the CdSe was etched for 30 min by sublimation in flowing Ar at 575°C. Stoichiometric sublimation of CdSe is possible because of the similar vapor pressures of Cd and Se.[3] The sample zone of the furnace was then reset to the growth temperature. After allowing the furnace temperature to stabilize at its new value, the source was pulled into the furnace with H_2 flowing at 8 cm^3/s.

The source temperature during growth was about 420°C. The sample was at a temperature of about 330°C; low enough to prevent excessive interdiffusion of the HgSe and CdSe. A variety of source and substrate temperatures near these values were used with essentially the same results. Growth times of from 10 min to 5 h were used for growing different epilayer thicknesses.

Growth morphology of the HgSe layers is visible in the SEM photographs of Figs. 2 and 3. Macroscopic steps were observed on the HgSe surface, whose direction is related to misorientation of the CdSe substrate. The height and distance between the steps increases with increasing growth thickness. The particular sample shown in Fig. 2 was one of the thinner epigrowths. Terraces up to almost 1 mm across have been observed after long growth times on well oriented substrates.

The cleaved edge in Fig. 3 shows that the HgSe layer is uniform and contains no macroscopic voids. The interface is smooth and looks abrupt on this scale.

Figure 4 shows 1.5 MeV $^4He^+$ ion backscatter spectra for (111) aligned and randomly oriented HgSe layers. The data

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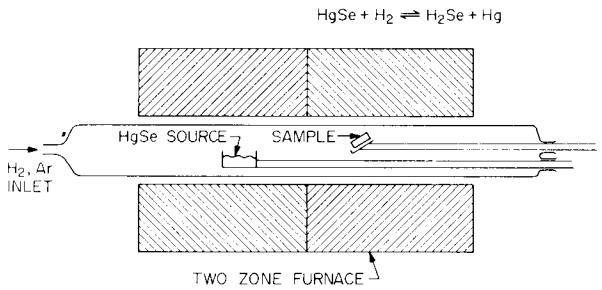

FIG. 1. Schematic diagram of the two-zone furnace used for H_2 transport CVD of HgSe on n-CdSe. The source and sample holder rods can be independently moved within the furnace. All hardware exposed to the carrier gas is made of quartz.

indicates that the layer is indeed epitaxial single-crystal. The (111) aligned channeling minimum yield is 15%, indicating fairly good crystal quality with some defects, possibly dislocations present.[4] The channeling spectrum for a sample grown on a substrate intentionally misoriented by 2° is also shown, and the minimum yeild is about 40%. The surface peak is also not evident, indicating *poor* epitaxy. Continuous films of HgSe are difficult to obtain on substrates misoriented by 3° or more.

There are two equivalent, but different orientations in which the threefold symmetric (111) planes of HgSe can grow on the sixfold CdSe basal plane. These differ in the order of the stacking sequence of the hexagonal close packed (111) planes. Equivalently, they differ by a 60° rotation about the [111] axis.

Laue back reflection x-ray patterns show the threefold symmetric pattern of the zincblende structure (111) plane. The threefold symmetry indicates that only one of the two possible HgSe orientations is present. This was true of all samples on which a Laue pattern was obtained.

Some property of the bulk CdSe, of the substrate preparation, or of the growth itself has caused a breaking of the sixfold symmetry seen by the HgSe as the epitaxial layer grows. Preliminary attempts to correlate the orientation of the HgSe with the small misorientation ($\approx 0.5°$) of the substrate have been unsuccessful. Another possible cause is defects in the CdSe substrate.

ELECTRICAL MEASUREMENTS

Grown samples were prepared for electrical measurements by masking with black wax and etching mesas with bromine–methanol solution. The mesa area was between 1×10^{-4} and 3×10^{-3} cm^2. Ohmic contacts were made to the substrates with In–Ag solder. Traditional techniques of current–voltage and photoresponse were used to measure the Schottky barrier heights.

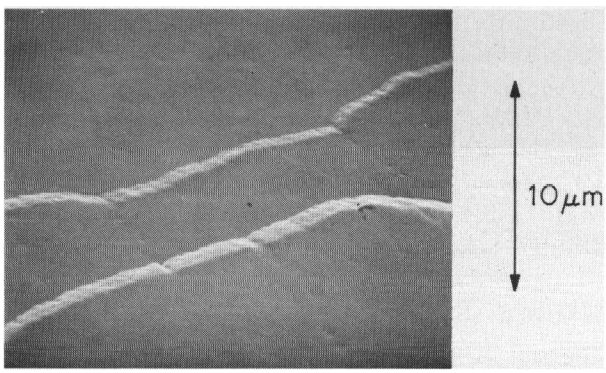

FIG. 2. SEM photograph of HgSe epitaxial layer surface.

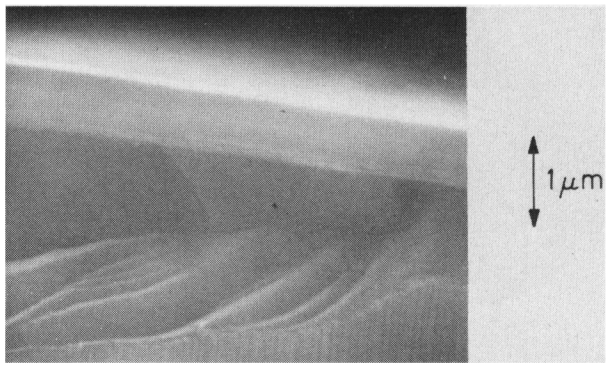

FIG. 3. SEM photograph of a cleaved cross section of HgSe on CdSe. The very bright, narrow region is the surface of the HgSe epilayer. Below that is the ≈8000-Å-thick, uniform HgSe layer. The lower 60% of the figure is the CdSe substrate.

Current–voltage curves are shown in Fig. 5, along with Au on n-CdSe Schottky barrier data for comparison. For pure thermionic emission current at room temperature, the slope of the curves should be about 1 decade of current change for each 60 mV increment of bias.[5] The Au on bromine–methanol etched CdSe diodes show a less than ideal slope. A cleaner, Au on air-cleaved CdSe interface shows the ideal slope, and a barrier height of 0.5 eV which is the same as the vacuum-cleaved value.[6] The HgSe data shown has a slope close to the ideal value and a barrier height of 0.73 eV.

Most HgSe diodes have an excess, nonthermionic emission current, which produces an I–V characteristic between that of the HgSe sample shown and the Au on chem-etched CdSe sample, both in slope and in magnitude. Leakage at the etched mesa periphery and defects at the heterostructure interface are possible sources of this current. The barrier height, as estimated using thermionic emission theory, is always greater than 0.6 eV.

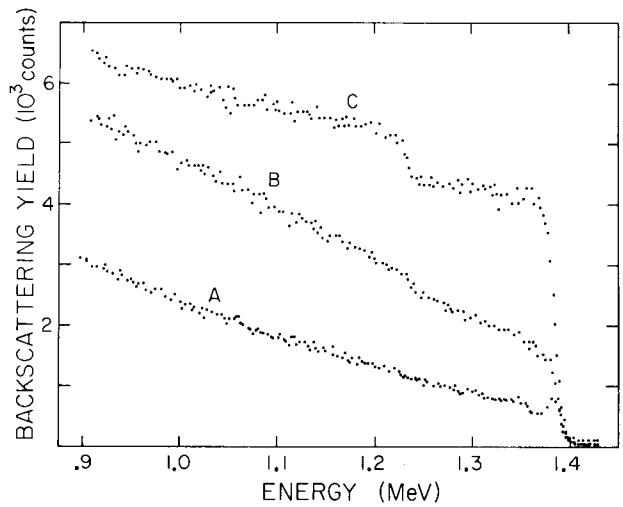

FIG. 4. 1.5 MeV $^4He^+$ channeling spectrum for HgSe epitaxial layer. Curve A is (111) aligned on well-oriented substrate. Curve B is (111) aligned on 2° misoriented substrate. Curve C is randomly aligned.

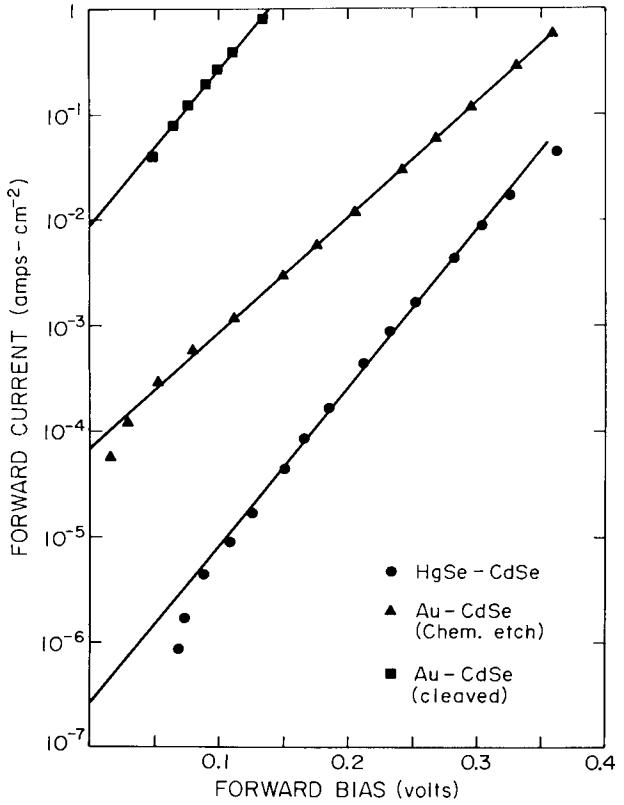

FIG. 5. Current–voltage characteristics for HgSe on n-CdSe and Au on n-CdSe Schottky barrier diodes. The barrier height for the HgSe/CdSe curve shown is 0.73 eV.

Photoresponse data is shown in Fig. 6. For HgSe on CdSe internal photoresponse, the photocurrent per incident photon R increases linearly with $(h\nu)$.[3] A square law is usually observed for metal-semiconductor Schottky barriers. This cube law is typical of photoemission from semiconductors into vacuum near the threshold for emission.[7] Data for a Au on chem-etched CdSe sample is provided for comparison.

The Schottky barrier height deduced from the photoresponse measurements is 0.73 ± 0.02 eV. It is reproducible even on samples which do not have ideal current–voltage characteristics. This number is probably the energy of the top of the HgSe valence band with respect to the bottom of the CdSe conduction band at the interface. It is not the Fermi level position normally measured by photoresponse, as the HgSe Fermi level is about 0.1 eV above the valence band maximum/conduction band minimum.

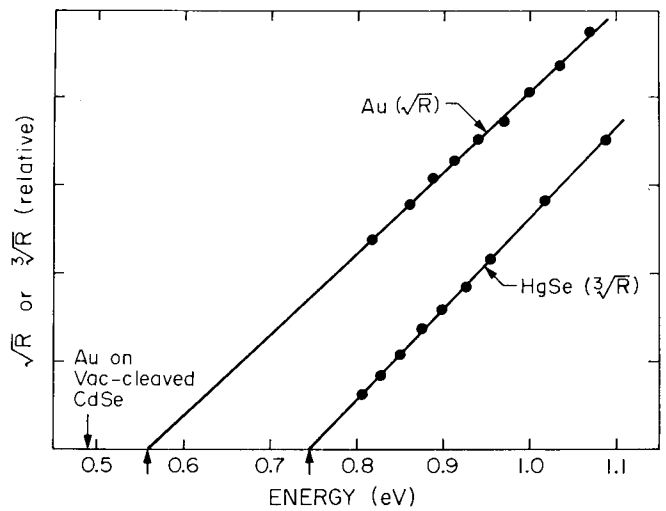

FIG. 6. Photoresponse measurements of HgSe on n-CdSe and Au on chemically etched n-CdSe Schottky diodes.

A few HgSe on n-CdSe samples were also made using the evaporation technique reported earlier.[8,9] These polycrystalline HgSe on n-CdSe diodes yielded poorly reproducible barrier heights roughly comparable with the Au on CdSe values. This lack of reproducibility prevented determining whether there was a small barrier height increase comparable with the 0.1 eV difference observed on other covalently bonded semiconductors. Similar problems occurred on some other materials, notably GaAs and CdTe.

DISCUSSION

A simple model of the heterostructure interface predicts that the valence band discontinuity at the interface is equal to the difference in vacuum ionization potential between the semiconductors. The ionization potential of the common III–V and II–VI materials is dependent primarily on the semiconductor anion.[10] One therefore expects that the valence band discontinuity for a heterostructure with a common anion would have a small valence band discontinuity at the interface. In fact, for $Al_xGa_{1-x}As/GaAs$, the valence band discontinuity is only 15% of the band gap difference. Extending this rule to the mercury-chalcogenides leads one to expect that the valence band discontinuity in a HgSe/CdSe heterostructure might be close to zero, giving a Schottky barrier on n-CdSe with barrier height close to the full bandgap of the CdSe. This is clearly not the case.

If we examine available vacuum photoemission data for HgSe, it is apparent that bulk HgSe does not have as large an ionization potential as would be expected from the common anion rule. In fact, the ionization potential is about 1.1 eV less than the potential for CdSe.[11,12] The CdSe band gap is 1.74 eV. Therefore, we expect a conduction band discontinuity of 0.64 eV. As the ionization potential data has an uncertainty of a couple of tenths of a volt, this is consistent with the experimental result of 0.73 eV.

It is also known that one cannot make CdSe significantly p-type. Compensating defects are created in the crystal as the Fermi level is pushed toward the lower half of the energy gap.[13] This may also prevent one from producing a Schottky barrier on n-CdSe with barrier height as large as one half of the band gap.

Neither of the above limitations exists for the case of HgTe on CdTe. The ionization potentials for the two materials are similar,[11,12] and CdTe can be made p-type. Both materials are of the zincblende structure, resulting in a true lattice-match for any orientation. We are presently attempting to grow HgTe on CdTe heterostructures with small enough interdiffusion to allow barrier measurements.

SUMMARY

By using simple, straightforward CVD techniques, we have grown a lattice-matched heterostructure which is also a

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[a] National Science Foundation Graduate Fellow.

[1] I. Lindau, P. W. Chye, C. M. Garner, P. Pianetta, C. Y. Su, and W. E. Spicer,
[6] C. A. Mead, Solid State Electron **9**, 1023 (1966).
[7] J. I. Pankove, *Optical Processes in Semiconductors* (Prentice-Hall, Englewood Cliffs, N. J., 1971), p. 290.
[8] J. S. Best, J. O. McCaldin, T. C. McGill, C. A. Mead, and J. B. Mooney, Appl. Phys. Lett. **29**, 433 (1976).
[9] R. A. Scranton, J. S. Best, and J. O. McCaldin, J. Vac. Sci. Technol. **14**, 930 (1977).
[10] J. O. McCaldin, T. C. McGill, and C. A. Mead, J. Vac. Sci. Technol. **13**, 802 (1976).
[11] N. J. Shevchik, J. Tejeda, M. Cardona, D. W. Laner, Phys. Status Solidi (b) **59**, 87 (1973).
[12] R. K. Swank, Phys. Rev. **153**, 844 (1967).
[13] F. A. Kroger (private discussion).